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THERMAL ANALYSIS OF EPOXY POWDER COATINGS

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ABSTRACT

Differential thermal analysis and thermogravimetric analysis have been used to study the identity of two different batches of epoxy coating powders. Differences in the cure-exotherms and in the reactivity of the different batches were shown to be a result of differences in the composition of a specific curing agent (amidine salt of a polycarbon acid) applied with the coating powders.

INTRODUCTION

Epoxy coating powders are widely used for decorative and anticorrosive coatings (1). Their specific properties, adhesion, mechanical and weather resistance, depend on the degree of cross linking. The cross linking reaction is a polyaddition reaction between epoxy groups of the resin and active H-atomes of curing agents, e. g. dicyandiamide. It starts at elevated temperatures and is exothermic, resulting in rather symmetrical DTA-peaks as shown in Fig. 1 (2 - 5). The reaction is promoted by an improved solubility of the curing agent as the reaction proceeds, and

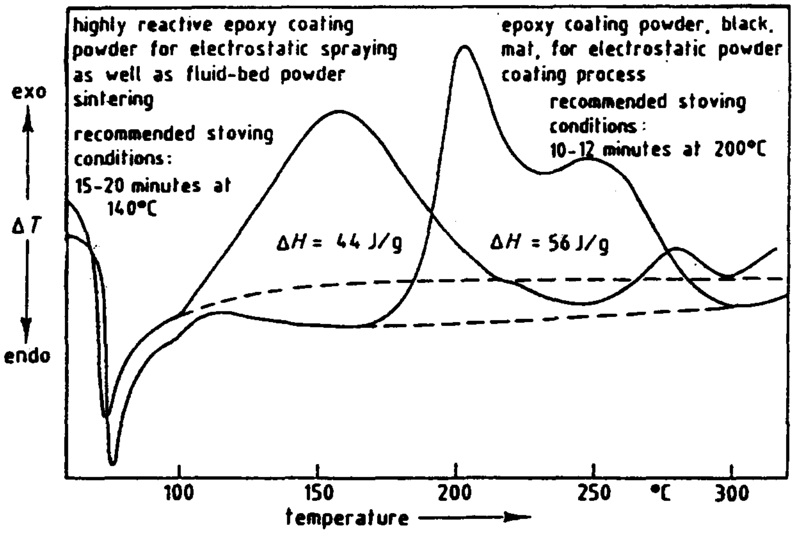

Fig. 1: DTA-curves of epoxy coating powders of different reactivities

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also by catalytic activities of tertiary amines formed during the reaction. Anhydrides are another species of curing agents. The primary reaction here is that with free OH-groups of the epoxy resin with ester formation, and only the active H-atom of the COOH-group formed this way can react with epoxy groups in a secondary cross linking reaction, and it is plausible that anhydrides are less reactive than amines.

For special effects, e. g. gloss regulation, combinations of different curing agents of different reactivities are used as shown in Fig. 1 (6). The curing reaction starts with the more reactive agent resulting in a coherent structure of partly cured material and molten, unreacted material. The partly cured component prevents levelling of the coating layer. In the course of further temperature rise the less reactive curing agent also reacts, which results in internal stresses and surface irregularities, namely mat surfaces.

The background for the present investigations was the question if the reason for coating defects with a commercial powder coating was bad epoxy powder or inadequate stoving temperature, and, as a matter of fact, the question of identity of contested and comparative coating powders for mat surface structures.

EXPERIMENTAL PROCEDURE AND MATERIALS

Thermogravimetric analysis was carried out using the Mettler system TA 3000, with a sample weight of 10 mg, heating rate of 10 K/min and cleansing gas 200 ml N_2/min up to 550 °C, and air at higher temperatures.

Differential thermal analysis was carried out using the Mettler system TA 2000, with a sample weight of 9 mg, heating rate 20 K/min and cleansing gas N_2 at a rate of 25 ml/min up to 300 °C.

The samples under test were epoxy powders of different batches designated as sample 1 (comparative sample) and 2 (contested sample). Thermogravimetric analysis showed slight differences in the quantitative composition of the two samples as listed in table 1:

For the investigation of the reactivity of the samples they were at first heated to the predetermined stoving temperature at a heating rate of 100 K/min, maintained there for a period of 10 minutes and cooled down to -30 °C at a rate of 20 K/min.

Table 1:

Reaction type	DTG-Peak		mass loss (%) or mass (%)	
	No	(°C)	sample 1	sample 2
thermal decomposition of EP-resin	1	435	59,0	62,0
combustion of carbon*)	2	550	10,1	9,7
sum of No 1 and 2			69,1	71,7
splitting of CO_2	3	710	12,8	11,9
amounting to $CaCO_3$			29,1	27,0
non identifiable residue			1,8	1,3

*) includes carbon residue from the thermal decomposition of the resin

After this stoving cycle the DTA was performed as described above to determine the residual heat of reaction.

The glass transition temperature T_g of the samples as a function of stoving conditions was determined from the DTA-curves as the point of intersection of the extrapolated baseline at the low temperature and the tangent to the curve at the inflection point.

For the interpretation of the curing reaction additional tests were carried out with model mixtures using a type 4 epoxy resin (epoxy equivalent weight 850 - 1000) and the curing agent as applied in the samples 1 and 2, with variable amounts of pyromellithic acid anhydride (PMDA).

The curing agent applied in the samples 1 and 2 was also characterized by DTA and ^1H- as well as ^{13}C-NMR-spectroscopy. According to the results of NMR two different curing agents which could have been applied with the samples 1 and 2 contained the same structural elements, namely a cyclic amidine and a symmetrical polycarbon acid, but with different relative amounts which could be calculated from certain assessments: With curing agent A, half the amount of the anhydride was present as compared to curing agent B. Consequently the DTA-curves of the curing agent A exhibited an additional melting peak at about 120 °C which can be attributed to the excess of the amidine (Fig. 2).

RESULTS AND DISCUSSION

Fig. 3 shows the DTA-curves of sample 2 as a function of stoving temperature. The DTA-curve of the unreacted material shows a

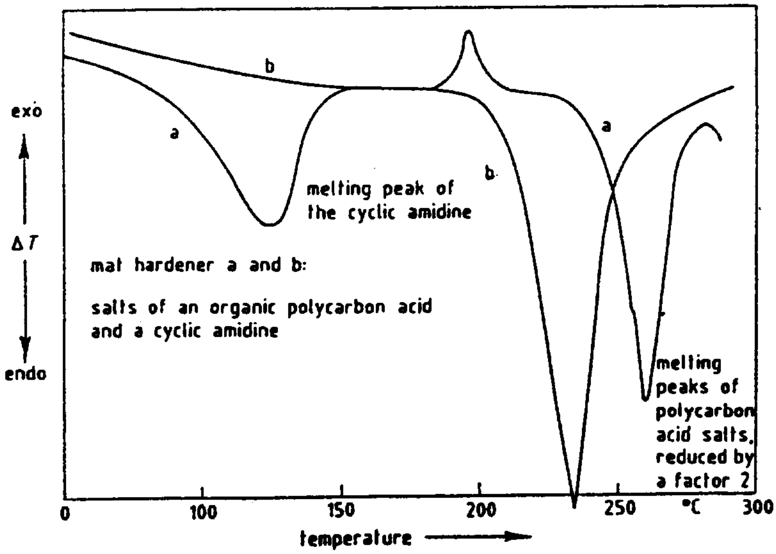

Fig. 2: DTA-curves of different mat hardeners

sharp peak at about 205 °C followed by a shoulder at about 240 °C. This behaviour indicates that different curing reactions are taking place, though the differences in reactivity are not so extreme as shown in Fig. 1, and from another observation with the gloss of the coatings (high gloss with low stoving temperatures, low gloss only at a stoving temperature of 200 °C) it was assumed that a special mat hardener was applied with the samples under test.

The total degree of conversion of the curing reactions was calculated from the total reaction enthalpy according to (5) $\alpha = \frac{\Delta H_o - \Delta H_t}{\Delta H_o}$, with ΔH_o = reaction enthalpy of the virgin powder, and ΔH_t = reaction enthalpy evolved to complete the curing after stoving for 10 minutes at the indicated temperatures. The results are shown in Fig. 4, and Fig. 5 demonstrates the relation between the degree of conversion and the glass transition temperature T_g.

Fig. 4 also gives the results of α as a function of the stoving temperature for sample 1. The corresponding DTA-curves are not presented here. It is apparent that sample 1 is more reactive than sample 2: To achieve a degree of conversion of 50 %, a temperature of 157 °C is needed for sample 1, but 162 °C for sample 2, and with a stoving temperature of 180 °C α is 0,91 for 1, and only 0,81 for 2.

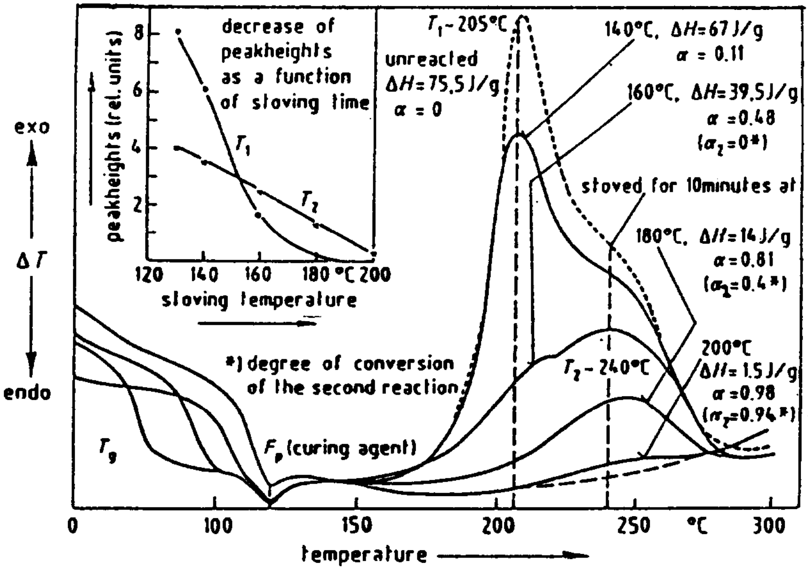

Fig. 3: DTA-curves of epoxy powder coatings as a function of stoving temperature of sample 2

The reason for these differences can be derived from Fig. 6: The DTA-curves of the virgin powder samples are different with respect to the asymmetry of the reaction peaks; the shoulder at 240 °C is less pronounced with sample 1. On the supposition that the total curing reaction consists of two different types of reaction, one of which starting at temperatures above 200 °C when the more reactive one has surpassed its peak, and assuming symmetrical shape of DTA-curves for each specific reaction type, one can calculate the relative proportions ΔH_1 and ΔH_2 of the

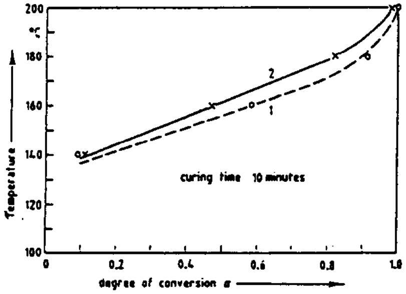

Fig. 4: Relation between stoving temperature and degree of conversion

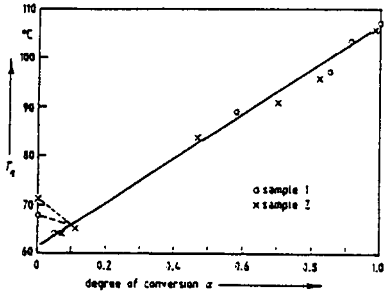

Fig. 5: Relation between the glass transition temperature T_g and the degree of conversion

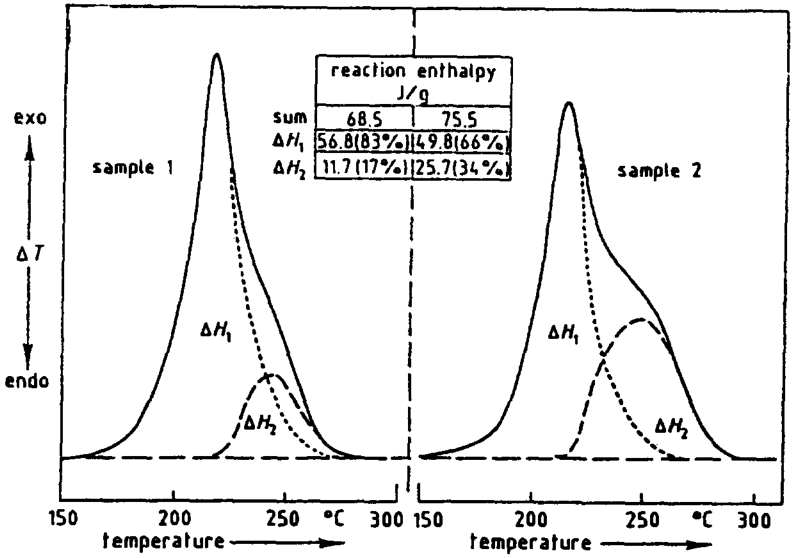

Fig. 6: Cure exotherms of different batches of epoxy coating powders

reactions. With sample 1, the less reactive part forms only about 17 % of the total reaction enthalpy, but 34 % with sample 2.

Fig. 3 also shows that the peak heights of the first reaction decreases more rapidly with increasing α than the second one. At a stoving temperature of 180 °C, the reaction peak has completely shifted to 240 °C and the second reaction is only completed for less than 50 %, α_2 being calculated from the ΔH_2 value of Fig. 6.

Fig. 7 compares the degrees of conversion obtained for a powder coating panel stoved at two different temperatures with those of the coating powder reacted in the DTA-crucible. Apparently the object temperature reached during the stoving of the panel was inferiour than indicated by the temperature measurement device of the oven, so the reaction peaks still indicate prevalent (160 °C) or measureable amounts (200 °C) of the first reaction, and the degrees of conversion are distinctly smaller.

From the results of different relative amounts of reaction enthalpies relating to curing reactions of different reactivities we conclude that two different curing agents have been applied in samples 1 and 2.

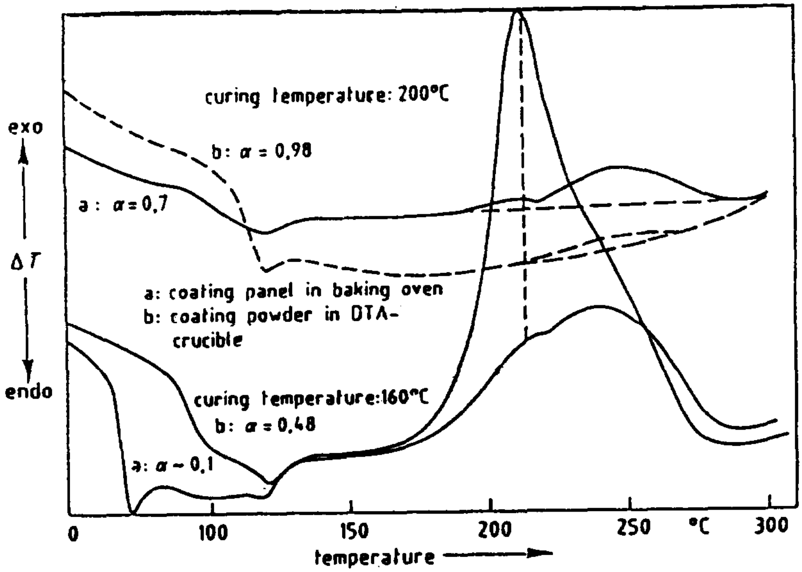

Fig. 7: Comparison of curing state of sample 2 at nominally equal temperatures

Assuming the same curing types in both curing agents, namely

- a higher reactive one including the amidine part of the hardener, (action of active hydrogen with epoxy-groups as well as catalytic reactions), and
- a less reactive one from the polycarbon acid or anhydride part,

but with different relative proportions, we can tentatively calculate the specific reaction enthalpies ΔH_r and ΔH_{1r} of the different reaction types, taking into account the differences in the organic binder content as obtained from the thermogravimetric analysis:

$0,83 \times \Delta H_r + 0,17 \times \Delta H_{1r} = 68,5/0,691$ J/g from sample 1
$0.66 \times \Delta H_r + 0,34 \times \Delta H_{1r} = 75,5/0.717$ J/g from sample 2

The solution of these equations gives the following specific reaction enthalpies (in brackets: values of Franiau (7) for comparable reactions):

for the higher reactive amine reaction ΔH_r = 93 J/g (90-105 J/g),
for the less reactive anhydride reaction ΔH_{1r} = 129 J/g (117-128 J/g).

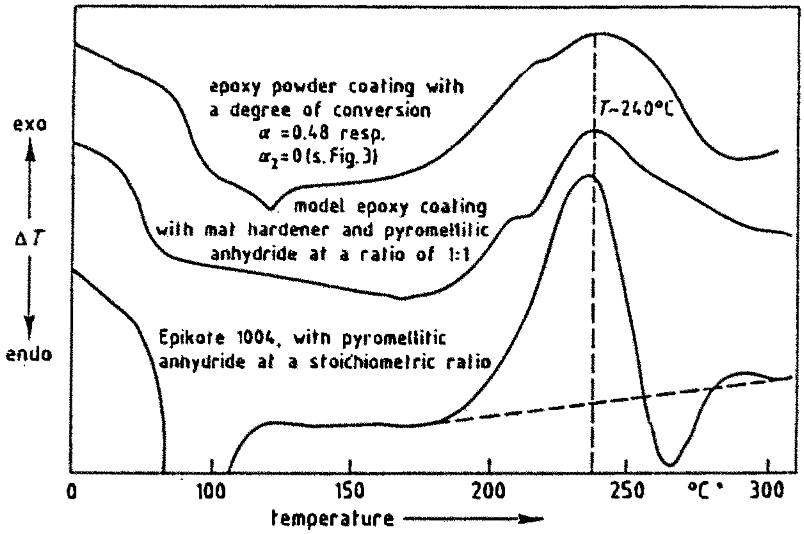

Fig. 8: DTA-curves of different model epoxy coating powders for demonstration of anhydride curing

On account of the good agreement of these specific reaction enthalpies with literature values the classification of the two different reaction types seems to be confirmed. Another proof for the less reactive curing reaction to correspond with the reaction of an anhydride can be derived from Fig. 8: The reaction peak of an epoxy resin with pyromellithic anhydride (PMDA) coincides with that of sample 2, and the reaction peak at about 240 °C is also prevalent with a mixture of the original mat hardener and PMDA.

A last test series has been carried out with model powders using curing agents with variable molar ratios of anhydride and cyclic amidine as listed in Fig. 9. The respective DTA-curves show that with increasing anhydride content, i. e. increasing prevalence of the less reactive reaction the DTA-peak shifts to a higher temperature and the peak height decreases. This corresponds to the results given in Fig. 3. Also a shoulder at the higher temperature side of the reaction peak is more distinct with higher contents of anhydride, this way confirming the observations given in Fig. 6 qualitatively.

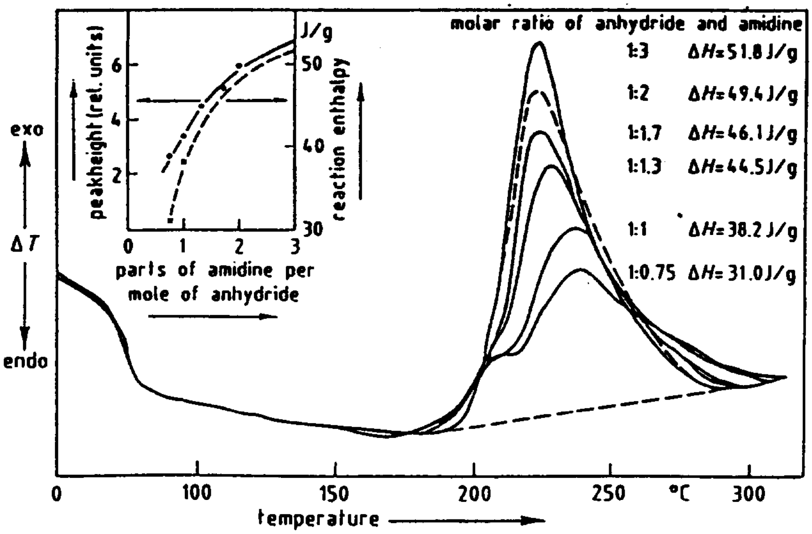

Fig. 9: DTA-curves of different model epoxy coating powders

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